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(54) **SYSTEM AND PROCESS FOR PRODUCING FUEL WITH A METHANE THERMOCHEMICAL CYCLE**

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CPC *C10J 1/20* (2013.01); *C07C 29/1518* (2013.01); *C10L 3/08* (2013.01)

(58) **Field of Classification Search**
CPC C10J 1/20; C07C 29/1518; C10L 3/08
See application file for complete search history.

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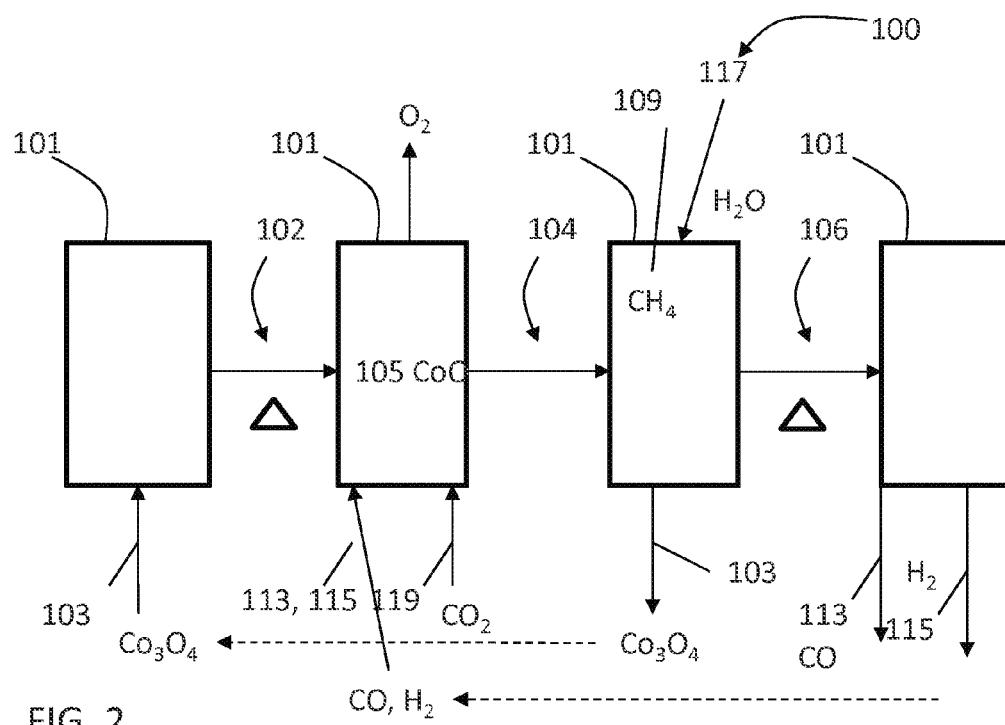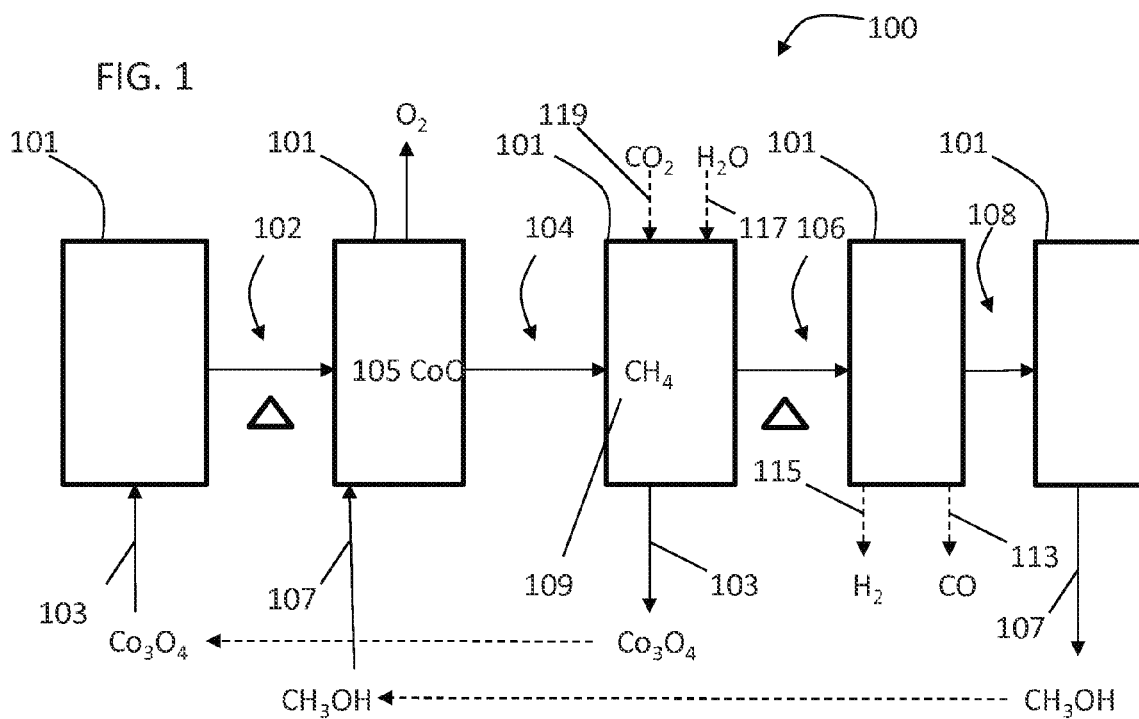
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(57) **ABSTRACT**

A thermochemical process and system for producing fuel are provided. The thermochemical process includes reducing an oxygenated-hydrocarbon to form an alkane and using the alkane in a reforming reaction as a reducing agent for water, a reducing agent for carbon dioxide, or a combination thereof. Another thermochemical process includes reducing a metal oxide to form a reduced metal oxide, reducing an oxygenated-hydrocarbon with the reduced metal oxide to form an alkane, and using the alkane in a reforming reaction as a reducing agent for water, a reducing agent for carbon dioxide, or a combination thereof. The system includes a reformer configured to perform a thermochemical process.

18 Claims, 1 Drawing Sheet

FIG. 1

100

101   101   119   101   101

O₂

CO₂ H₂O

102   104   117 106 108

105 CoO   CH₄

△   △

109   115   113

103   107   103   H₂ CO   107

Co₃O₄   Co₃O₄

CH₃OH   CH₃OH

100

117

101   101   109   101

O₂   H₂O

102   104   106

105 CoO   CH₄

△   △

103   113, 115 119 103   H₂

Co₃O₄   CO₂ Co₃O₄   113 115

CO, H₂   CO

FIG. 2

SYSTEM AND PROCESS FOR PRODUCING FUEL WITH A METHANE THERMOCHEMICAL CYCLE

PRIORITY

The present disclosure claims priority and benefit of U.S. Provisional Patent Application No. 61/859,811, titled "SYSTEM AND PROCESS FOR PRODUCING FUEL WITH A METHANE THERMOCHEMICAL CYCLE" and filed Jul. 30, 2013, the entirety of which is incorporated by reference.

STATEMENT CONCERNING FEDERALLY-SPONSORED RESEARCH

The present invention was made in connection with Government support under contract number DE-SC0004729 awarded by the Department of Energy. The Government may have certain rights with the invention.

FIELD OF THE INVENTION

The present invention is directed to processes and systems for producing fuel by using a methane thermochemical cycle. More specifically, the present invention relates to chemically reducing an oxygenated-hydrocarbon that is used to then promote the splitting of water and/or carbon dioxide, producing fuel. The oxygenated hydrocarbon is regenerated and completes the thermochemical cycle.

BACKGROUND OF THE INVENTION

Most of the energy consumed in the world today is "stored solar energy" in the form of fossil fuels, such as petroleum, natural gas, and coal. Fossil fuels, however, are finite and their combustion has been tied to an increase in the amount of carbon dioxide in the atmosphere and other pollutants in the environment. Their limited availability also has national security and economic implications.

Solar and nuclear energy are not limited in the same manner as fossil fuels. They can provide viable long-term persistent energy options and be an environmentally advantageous, long-term alternative to fossil fuels. Such sources can produce hydrogen from water, which can be used as an independent, clean-burning fuel.

Thermochemical processes for converting solar or nuclear energy into fuels are potentially more straightforward, efficient, and less costly than using electric power to electrolyze water. Thermochemical cycles utilize high-temperature heat and a series of chemical reactions to produce fuels. Thermochemical water-splitting cycles utilize a series of chemical reactions with the overall reaction $H_2O \rightarrow H_2 + \frac{1}{2}O_2$. Thermochemical carbon dioxide-splitting cycles utilize a similar series of chemical reactions with the overall reaction $CO_2 \rightarrow CO + \frac{1}{2}O_2$. All of the other chemicals are recycled within the process.

Recent solar thermochemical research has focused on two-step metal oxide cycles that alternately thermally reduce a metal oxide, such as magnetite (Fe_3O_4) to wustite (FeO), producing oxygen, and then oxidize the metal oxide with water or carbon dioxide to produce hydrogen or carbon monoxide, respectively. The metal oxide is typically cycled between the high temperature thermal reduction step and a lower temperature re-oxidation step. For example, cerium oxide is a metal oxide that has received notable attention. The metal oxide cycles are attractive in that they involve only two chemical steps. However, they require temperatures of at least

1400° C. for reasonable efficiencies, even with the addition of other dopants to the metal oxides to lower the required thermal reduction temperature. These high temperatures preclude the use of nuclear power and severely impact the design and efficiency of solar collection hardware.

To split water or carbon dioxide at lower temperatures, known nuclear driven thermochemical cycle work has centered on cycles that involve the decomposition of sulfuric acid, with the sulfur-iodine and hybrid sulfur processes receiving significant attention. A number of thermochemical cycles have been proposed; however, they rely upon sulfur oxides or other corrosive or hazardous materials, require substantial amounts of electrical power, have failed to be operational, produce corrosive and/or toxic chemicals, are harmful to the environment, create safety concerns, or a combination thereof.

A system and process for producing fuel with a methane thermochemical cycle that do not suffer from one or more of the above drawbacks would be desirable in the art.

BRIEF DESCRIPTION OF THE INVENTION

In an embodiment, a thermochemical process includes reducing an oxygenated-hydrocarbon to form an alkane and using the alkane in a reforming reaction as a reducing agent for water, a reducing agent for carbon dioxide, or a combination thereof.

In another embodiment, a thermochemical process includes reducing a metal oxide to form a reduced metal oxide, reducing an oxygenated-hydrocarbon with the reduced metal oxide to form an alkane, and using the alkane in a reforming reaction as a reducing agent for water, a reducing agent for carbon dioxide, or a combination thereof.

In another embodiment, a system includes a reformer configured to perform a thermochemical process. The thermochemical process includes reducing an oxygenated hydrocarbon to form an alkane and using the alkane in a reforming reaction as a reducing agent for water, a reducing agent for carbon dioxide, or a combination thereof.

Other features and advantages of the present invention will be apparent from the following more detailed description of the preferred embodiment, taken in conjunction with the accompanying drawings which illustrate, by way of example, the principles of the invention.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 schematically depicts an embodiment of a system performing an embodiment of a four-step process, according to the disclosure.

FIG. 2 schematically depicts an embodiment of a system performing an embodiment of a three-step process, according to the disclosure.

DETAILED DESCRIPTION OF THE INVENTION

Provided is a system and process for producing fuel with a methane cycle. Embodiments of the present disclosure, for example, in comparison to processes and systems not including one or more of the features disclosed herein, permit operation that is devoid of one or more undesirable intermediates (for example, being devoid of or substantially devoid of SO_2, metal sulfate, dopants, catalysts, or combinations thereof), permit solar flux to directly illuminate a metal oxide, permit water and/or carbon dioxide to be split, permit fuel to be produced (for example, hydrogen, carbon monoxide, or a

combination thereof, or even methanol in one variant of the process), or a combination thereof.

Referring to FIGS. **1** and **2**, a process **100**, according to the disclosure, is a four-step process (see FIG. **1**) or a three-step process (see FIG. **2**) capable of producing fuel through use of a methane (or alkane) cycle. The thermochemical process **100** includes reducing, such as, thermally-reducing (step **102**) with solar or nuclear heat, for example, a metal oxide **103** to form a thermally-reduced metal oxide **105** and reducing (step **104**) an oxygenated-hydrocarbon **107** (for example, methanol, ethanol, butanol, propanol, any other suitable oxygenated-hydrocarbon, or a combination thereof, or syngas (mixture of CO **113** and H2 **115**) as in FIG. **2**) with the thermally-reduced metal oxide **105** to form an alkane, such as methane **109**, capable of being used as an intermediate reactant for further processing.

The thermochemical system **101** is configured for the thermochemical process **100**. In one embodiment, the thermochemical system **101** produces fuel (for example, as H_2, CO, CH_3OH, or a combination thereof) from the thermochemical process **100** in conjunction with a persistent or substantially persistent energy source, such as a solar power system or a nuclear power system.

The thermally-reducing (step **102**) and the reducing (step **104**) are concurrent, substantially concurrent, or sequential. The thermally-reducing (step **102**) and the reducing (step **104**) produce a re-oxidized metal oxide **103**. In contrast to other processes, the re-oxidized metal oxide **103** is not directly re-oxidized with water or carbon dioxide to produce hydrogen or carbon monoxide directly. Instead, the re-oxidized metal oxide **103** is produced by reducing the oxygenated-hydrocarbon **107** (as shown in FIG. **1**) and/or syngas **115** (as shown in FIG. **2**).

Although not intending to be bound by theory, in an embodiment with the oxygenated-hydrocarbon **107** being methanol, due to the oxygen binding energy of methanol, for example, being less than half that of the oxygen-hydrogen bond in water **117** or the oxygen-carbon monoxide bond in carbon dioxide **119**, the metal oxide **103** is selected to be more readily thermally-reduced (step **102**), for example, at temperatures less than otherwise required for a two-step process. The reduced metal oxide **105** splits CH_3OH rather than CO_2 or H_2O directly. In comparison, to thermally reduce cerium oxide ($2CeO_2 \rightarrow Ce_2O_3 + \frac{1}{2}O_2$) with products and reactants at their standard states requires temperatures in excess of 2300° C. Similarly, in reducing magnetite to wustite ($Fe_3O_4 \rightarrow 3FeO + \frac{1}{2}O_2$), temperatures in excess of 2700° C. are used. However, selecting cobalt oxide as the metal oxide **103**, according to an embodiment of the present disclosure, for example, permits the metal oxide **103** to be reduced at temperatures of less than 1000° C. ($Co_3O_4 \rightarrow 3CoO + \frac{1}{2}O_2$) and the thermally-reduced metal oxide **105**, being thermally-reduced cobalt oxide, is thermodynamically capable of being re-oxidized by methanol to produce the methane **109** at temperatures less than about 380° C. ($3CoO + CH_3OH \rightarrow CH_4 + Co_3O_4$).

In one embodiment, the metal oxide **103** is hematite/magnetite (Fe_2O_3/Fe_3O_4), having a methanol reduction reaction to the methane **109** that is thermodynamically more favorable than that of cobalt oxide; however, in this embodiment, the thermal reduction (step **102**) requires temperatures in excess of 1360° C. in air. Other metal oxides are capable of being used to tailor thermodynamic and kinetic properties by using mixed oxides. When selecting the metal oxide **103** without consideration of being more readily thermally-reduced (step **102**), for example, when selecting cerium oxide or magnetite, a higher extent of reduction is achieved by the use of a vacuum

or sweeping with an inert or otherwise oxygen-free gas. Such measures decrease system-level efficiency and temperatures, however, a temperature of at least 1400° C. is still required thermodynamically. These higher temperatures for thermally-reducing (step **102**) the metal oxide **103** result in significant materials issues and low solar efficiency. Also, advanced nuclear heat sources cannot provide these temperatures.

In one embodiment, the thermochemical process **100** includes producing carbon monoxide **113** and hydrogen **115** from the methane **109** and water **117** (known as steam reforming), methane **109** and carbon dioxide **119** (known as dry reforming), or a combination thereof. At least a portion of the methane **109** is reformed with water **117** and/or carbon dioxide **119** using heat, for example, from a solar power system and/or nuclear power system, to produce the carbon monoxide **113** and the hydrogen **115**. Because reforming the methane **109** produces more moles of the hydrogen **115** or the carbon monoxide **113** compared to what is needed to synthesize the methanol used to generate the methane **109**, the net reaction is the production of the hydrogen **115**, carbon monoxide **113**, or a product syngas, including the hydrogen **115** and the carbon monoxide **113**. In one embodiment, the heating value of the product syngas is increased compared to the methane **109** (for example, by between 25% and 30%, when the water **117** and the carbon dioxide **119** are being reformed, respectively).

Referring specifically to FIG. **1**, in one embodiment, the process **100** includes water splitting, for example, as is illustrated in Table 1, using cobalt oxide as the metal oxide **103** for producing the thermally-reduced metal oxide **105**, to reduce the oxygenated-hydrocarbon **107**, specifically methanol. In this embodiment, the process **100** includes reactions in a four-step metal oxide-methane cycle in which producing a fuel (step **106**), such as the hydrogen **115**, in part, synthesizes the methanol (step **108**) that is fed back to the reducing (step **104**).

TABLE 1

Step	Reaction	ΔH, kcal @25° C.	Temperature, ° C.
102	$Co_3O_4 \rightarrow 3CoO + 1/2O_2$	46.89	>800° C.
104	$3CoO + CH_3OH \rightarrow Co_3O_4 + CH_4$	−16.68	<300° C.
106	$H_2O + CH_4 \rightarrow CO + 3H_2$	49.21	>800° C.
108	$CO + 2H_2 \rightarrow CH_3OH$	−21.62	200-300° C.
Net	$H_2O \rightarrow H_2 + 1/2O_2$	57.8	

In one embodiment of the process **100**, the efficiency of performing the thermal reduction (step **102**) at 900° C., the producing of the hydrogen **115** (step **106**) at 800° C., the reducing of the oxygenated-hydrocarbon **107** (step **104**) at 300° C., and the re-producing of the methanol (step **108**) at 300° C. is 63.8%; assuming full recuperation of sensible heat from the reduced cobalt oxide and reformed syngas, and with no heat recuperation the cycle efficiency is 46.9%.

TABLE 2

Step	Reaction	ΔH, kcal @25° C.	Temperature, ° C.
102	$Co_3O_4 \rightarrow 3CoO + 1/2O_2$	46.89	>800° C.
104	$3CoO + CH_3OH \rightarrow Co_3O_4 + CH_4$	−16.68	<300° C.
106	$CO_2 + CH_4 \rightarrow 2CO + 2H_2$	59.04	>800° C.
108	$CO + 2H_2 \rightarrow CH_3OH$	−21.62	200-300° C.
Net	$CO_2 \rightarrow CO + 1/2O_2$	67.63	

In one embodiment, the process **100** includes the oxygenated-hydrocarbon **107**, specifically the methanol, being a product, such as, a product fuel as is shown in Table 3 and FIG. **1**. In this embodiment, the carbon dioxide **119** and the water **117** are reformed in the presence of methane to produce syngas, which is then used to synthesize methanol **107**.

TABLE 3

Step	Reaction	ΔH, kcal @25° C.	Temperature, ° C.
102	$3Co_3O_4 \rightarrow 9CoO + 3/2O_2$	140.67	>800° C.
104	$9CoO + 3CH_3OH \rightarrow 3Co_3O_4 + 3CH_4$	−50.04	<300° C.
106	$CO_2 + 2H_2O + 3CH_4 \rightarrow 4CO + 8H_2$	157.46	>800° C.
108	$4CO + 8H_2 \rightarrow 4CH_3OH$	−86.48	200-300° C.
Net	$CO_2 + 2H_2O \rightarrow CH_3OH + 3/2O_2$	161.61	

The embodiments of the process **100** described in Tables 1-3 show that by adjusting the relative amounts of the carbon dioxide **119** and the water **117** fed in the producing of the carbon monoxide **113** and the hydrogen **115** (step **106**), syngas is capable of being produced with any ratio of the carbon monoxide **113** to the hydrogen **115**. In one embodiment, some heat for the producing of the hydrogen **115** (step **106**) or the thermally-reducing of the metal oxide **103** (step **102**) is partially provided from the reducing of the oxygenated-hydrocarbon **107** (step **104**) and/or the re-producing of the methanol (step **108**).

According to embodiments of the process **100**, all of the products and intermediate reactants shown in Tables 1-3 are readily separable. Oxygen gas produced in the thermally-reducing of the metal oxide **103** (step **102**) is capable of being separated from the thermally-reduced metal oxide **105**.

In one embodiment, the cobalt oxide reduction reaction in the thermally-reducing of the metal oxide **103** (step **102**) is performed in air at temperatures down to about 940° C. In another embodiment, the temperature is lowered to about 800° C. by using an inert gas, such as nitrogen, argon, steam, or a combination thereof. These temperatures enable the use of heat pipes and packed-bed reactors constructed from conventional metals, in addition to other high-temperature materials.

The methane **109** produced in the reducing of the oxygenated-hydrocarbon **107** (step **104**) is capable of being separated. In one embodiment, the reducing of the oxygenated-hydrocarbon **107** (step **104**) is performed with the oxygenated-hydrocarbon **107** in the gas phase and any of the oxygenated-hydrocarbon **107** carried over being separated from the methane **109** by condensation.

The reducing of the oxygenated-hydrocarbon **107** (step **104**) is performed at a thermodynamically favorable temperature, for example, less than about 380° C., for the reaction $3CoO + CH_3OH(g) \rightarrow CH_4(g) + Co_3O_4$. This embodiment is susceptible to side reactions resulting in the formation of the water **117** or the carbon dioxide **119**, instead of the methane **109**. In one embodiment, the reducing of the oxygenated-hydrocarbon **107** (step **104**) is performed with few or without any side reactions, for example, by performing the reducing of the oxygenated-hydrocarbon **107** (step **104**) at as low a temperature as possible and/or by using a catalyst (not shown) such as nickel, platinum, rhodium, copper, palladium, other suitable catalysts, or a combination thereof.

In one embodiment, the process **100** includes photochemical stimulation to the reducing of the oxygenated-hydrocarbon **107** (step **104**), for example, as $CH_3OH + h\nu \rightarrow$

$CH_4 + \frac{1}{2}O_2$. Because the oxygen binding energy in the oxygenated-hydrocarbon **107** is significantly less than for the water **117** or the carbon dioxide **119**, a much higher fraction of the solar spectrum is capable of directly reducing methanol **107** to the methane **109**, than for the water **117** or the carbon dioxide **119** photolysis reactions, thereby permitting an embodiment with the thermally-reducing of the metal oxide **103** (step **102**) and the reducing of the oxygenated-hydrocarbon **107** (step **104**) being combined.

In one embodiment, the reducing of the oxygenated-hydrocarbon **107** (step **104**) is in a single syngas reduction step in the process **100**, as is shown in the three-step embodiment depicted in FIG. **2**. FIG. **2** specifically shows a carbon dioxide splitting three-step cycle corresponding to Table 4. For water splitting, the reducing of the oxygenated-hydrocarbon **107** (step **104**) proceeds according to the following reaction, $3CoO + CO + 2H_2 \rightarrow Co_3O_4 + CH_4$, as part of a three-step metal oxide-methane cycle with the hydrogen **115** produced, for example, as a product fuel.

TABLE 4

Step	Reaction	ΔH, kcal @25° C.	Temperature, ° C.
102	$Co_3O_4 \rightarrow 3CoO + 1/2O_2$	46.89	>800° C.
104	$3CoO + CO_2 + 3H_2 \rightarrow Co_3O_4 + CH_4 + H_2O$	−28.47	<300° C.
106	$CH_4 + H_2O \rightarrow CO + 3H_2$	49.21	>800° C.
Net	$CO_2 \rightarrow CO + 1/2O_2$	67.63	

The re-oxidation of the reduced metal oxide using syngas **115** (step **104**) for hydrogen production is thermodynamically favorable with products and reactants at their standard state at temperatures less than about 300° C. However, because the reaction results in fewer moles in the gas phase, increasing reaction pressure improves the reaction potential and increases the temperature range in a manner similar to conventional methanol synthesis.

The process **100** includes any suitable additional steps. In one embodiment, the process **100** includes producing a synthesized oxygenated-hydrocarbon from at least a portion of the carbon monoxide **113** and the hydrogen **115**. In a further embodiment, the process **100** includes using the synthesized oxygenated-hydrocarbon as the oxygenated-hydrocarbon **107** for further reduction. Additionally or alternatively, in one embodiment, the process **100** includes using the re-oxidized metal oxide **103** for further thermal reduction and/or further cycles.

While the invention has been described with reference to a preferred embodiment, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiment disclosed as the best mode contemplated for carrying out this invention, but that the invention will include all embodiments falling within the scope of the appended claims.

What is claimed is:

1. A thermochemical process, comprising:
    reducing an oxygenated-hydrocarbon with reduced metal oxide to form an alkane; and
    using the alkane in a reforming reaction as a reducing agent for water, a reducing agent for carbon dioxide, or a combination thereof;
    wherein the process is devoid of metal sulfate.

2. The process of claim **1**, wherein the reducing of the oxygenated-hydrocarbon produces a re-oxidized metal oxide.

3. The process of claim **1**, further comprising producing carbon monoxide and hydrogen from the alkane, the water, the carbon dioxide, or a combination thereof.

4. The process of claim **3**, further comprising producing a synthesized oxygenated-hydrocarbon from at least a portion of the carbon monoxide and the hydrogen.

5. The process of claim **4**, further comprising using the synthesized oxygenated-hydrocarbon for further re-oxidation a reduced metal oxide.

6. The process of claim **3**, wherein the producing of the carbon monoxide and the hydrogen is at a temperature of less than 1000° C.

7. The process of claim **3**, wherein the producing of the carbon monoxide or the hydrogen is at a temperature of less than 1000° C.

8. The process of claim **1**, wherein the process is devoid of SO_2.

9. The process of claim **1**, wherein the process is devoid of dopants.

10. The process of claim **1**, wherein the process is devoid of catalysts.

11. The process of claim **1**, wherein the process includes at least three steps.

12. The process of claim **1**, wherein the process includes at least four steps.

13. The process of claim **1**, further comprising promoting splitting of one or both of the water and the carbon dioxide by one or both of photochemical and electrochemical stimulus.

14. The process of claim **13**, wherein the promoting of the splitting is at a temperature of less than 1000° C.

15. The process of claim **1**, wherein the alkane is methane.

16. The process of claim **1**, wherein the process produces fuel.

17. The process of claim **1**, wherein the fuel is hydrogen, carbon monoxide, syngas, methanol, ethanol, butanol, propanol, or a combination thereof.

18. A thermochemical process, comprising:

reducing a metal oxide to form a reduced metal oxide;

reducing an oxygenated-hydrocarbon with the reduced metal oxide to form an alkane; and

using the alkane in a reforming reaction as a reducing agent for water, a reducing agent for carbon dioxide, or a combination thereof.

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